

MODELING OF COAL PYROLYSIS UNDER THE CONDITIONS OF AN ENTRAINED PHASE REACTOR

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INTRODUCTION

Experimental laboratory work has shown that yield and quality of liquid products from coal pyrolysis can be controlled and optimized to a certain extent by suitable coaction of the primary thermal coal decomposition reactions and the secondary cracking or hydrocracking of the volatiles. The results indicate that favorable process conditions are provided in an entrained phase transport reactor which enables high heating rates for fast primary coal pyrolysis together with optimum residence time of the volatiles for secondary cracking and hydrocracking in the heated reactor zone. From that point of view the question arises how thermal coal decomposition can be described at high heating rates and whether transport limiting processes are involved in the overall reaction step. Especially for reactor design it is necessary to clarify to what extent experimental kinetic data gained at low heating rates can be applied to heating conditions like in a fluidized bed or in an entrained phase reactor.

KINETIC EXPERIMENTS

Low Heating Rates - Thermobalance Experiments

For experimental investigations of the influence of heating rate on the kinetics of coal pyrolysis three different types of equipment have been used as shown in Fig. 1. In previous work at low heating rates the course of product formation - total weight loss, tar, and gas - depending on temperature was measured in non-isothermal experiments in a thermobalance /1/. The low heating rate of some K/min in the thermobalance allows, beside the recording of the decrease in mass of the coal sample, a continuous analysis of the product gases (including detection of H_2O) and, by difference between total mass loss and total gas formation, the calculation of tar formation.

The mass loss curve as well as the curves for the different gaseous components show a certain structure which indicates that the volatiles are liberated in several single reactions for each component. The reactions can in a first order regarded as a set of independent parallel reactions. This model of non-isothermal reaction kinetics allows a mathematical description of product formation. With the model equations the measured curves can be described by fitting activation energy E and frequency factor k_0 .

High Heating Rates - Grid Heater Experiments

The verification of the measured kinetic data at high heating rates has been carried out in experiments with a grid heater and with a Curie-point pyrolysis equipment. Schwandtner /2/ used a grid heater in the vacuum chamber of a time of flight mass spectrometer and applied heating rates up to 3000 K/s. The fast response signal of the mass spectrometer enabled kinetic measurements at high heating rates. According to theoretical calculations with the equations describing the non-isothermal reaction kinetics Schwandtner found a significant influence of the heating rate on the gas formation curves, which were shifted towards higher temperatures, respectively towards later times. But additionally, the gas release was shifted with rising particle

size as shown in Fig. 2. For coal grains exceeding 0.4 mm in diameter furthermore a tailing at the end can be noticed. With further enlargement of the grain size up to 1 mm and more the gas formation rate becomes independent of time. This means a reaction order of 0, which expresses the increasing influence of heat conductivity at these experimental conditions. This effect can be explained by the assumption that the heat transfer into the grain limits at certain heating rate and particle size the overall pyrolysis reaction. By a simple calculation of the temperature profile in the coal particle and integration of the total gas formation in the particle on the basis of a shell model the measured curves can be fitted as shown in Fig. 2.

High Heating Rates - Curie-Point Experiments

By using a different heating technique similar investigations were carried out with a pressurized Curie-point equipment which allows high heating rates above 10,000 K/sec and by that nearly isothermal pyrolysis experiments /3/. The method for measuring the critical particle diameter above which the transition from chemical reaction control to transport rate control occurs, involves measuring the yield of pyrolysis products, mainly the tar, at incomplete coal decomposition reaction. At a given heating rate and pressure, mass loss is independent of particle diameter at low particle size. By increasing particle size a distinct drop in the mass loss is noted as shown in Fig. 3, indicating that mass and/or heat transfer effects inhibit the escape of the volatiles from the particle. The critical particle diameter can, therefore, be determined by the change in the trend of mass loss versus particle size and finally plotted as function of heating rate (Fig.4).

HEAT TRANSFER CALCULATIONS

In order to achieve a more precise separation between the experimentally measured mass and enthalpy transport effects and their relevance for the measurement of kinetic pyrolysis data, model calculations were performed. The model assumes a spherical coal grain with its surface heated time dependently. It includes reaction enthalpies uniformly distributed in the coal particle. Intraparticle temperature profiles are then calculated using boundary conditions specific to the different heating methods in each apparatus.

The result of a calculation reproducing the conditions in the Curie-point measurements at a heating rate of 6.000 K/s for grain sizes at and above the critical radius (0.1 mm and 2 mm respectively) is shown in Fig. 5. The temperature profiles show quite clearly the existence of the measured critical diameters being in a first approximation a result of heat conduction within the coal. These radii are the limit up to which the heating rate can cause intra particle temperature gradients. The thermobalance uses a heating rate of 3 K/s, slow enough to prevent temperature gradients within the particle. With grain sizes below 0.1 mm also the pyrolysis yields of the Curie-point apparatus at heating rates up to 10,000 K/s may be evaluated without having to account for non-isothermal coal grains (Fig. 6).

As a consequence, looking at temperature profiles in a grain with the surface heated up instantaneously, as an upper limit for the conditions in an entrained phase reactor, internal temperature profiles die out after some ten milliseconds. These are time increments of the order of magnitude needed to reach thermal equilibrium between gas and coal within the very beginning of the reaction tube. The description of reaction kinetics in such a reactor type should therefore be possible on the basis of experimental data gained with the thermobalance and the curie point apparatus.

REFERENCES

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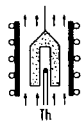
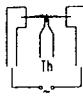

apparatus	thermobalance	wire-net-technique	Curie-point-technique
			
sample size	mg	1,500	10
heating rate	K/s	0.05	200-1,500
final temperature	°C	1,000	1,000
			5 10,000 adjustable isothermal experiments
results	kinetics of product formation E, k_0, n, V_0 for H_2, CO_2, C_2H_4 , BTX and tar product yield	kinetics of particle swelling from high speed camera studies	kinetics of product formation E, k_0, n, V_0 for H_2, CO_2, C_2H_4 , BTX and tar product yield

Fig. 1: Laboratory Equipment for Pyrolysis Experiments

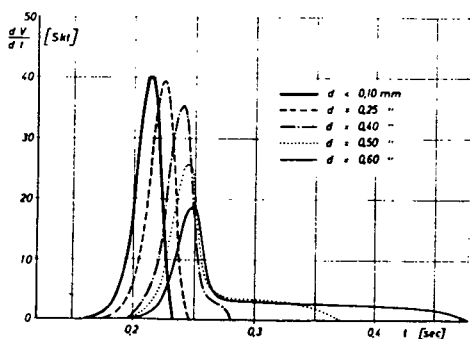


Fig. 2: Calculated Devolatilization Curves ($E = 240$ kJ/mol, $k_0 = 10^{11} \text{ min}^{-1}$)

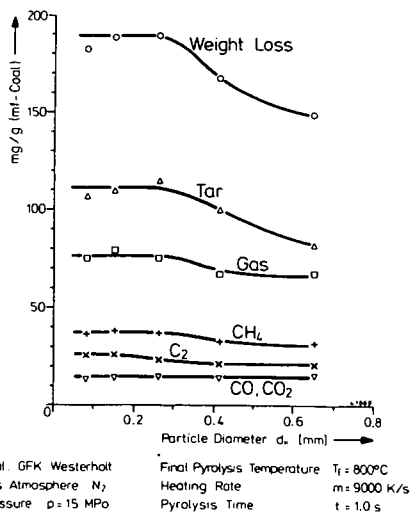


Fig. 3: Influence of Particle Size at High Heating Rates

Gasflammkohle Westerholt
pyrolysis temperature 800°C

- 0.01 MPa N₂
- 5 and 15 MPa N₂
- 10 and 15 MPa H₂

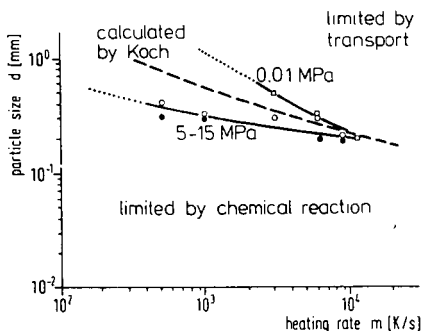


Fig. 4: Reaction Rate Limiting Step Depending on Heating Rate and Pressure

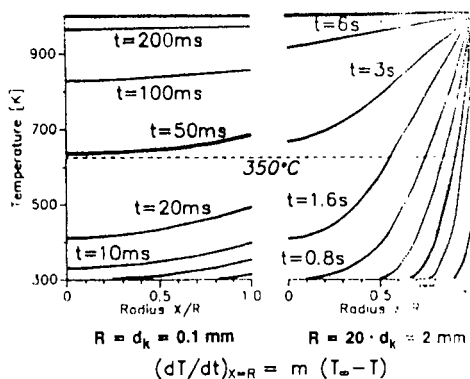
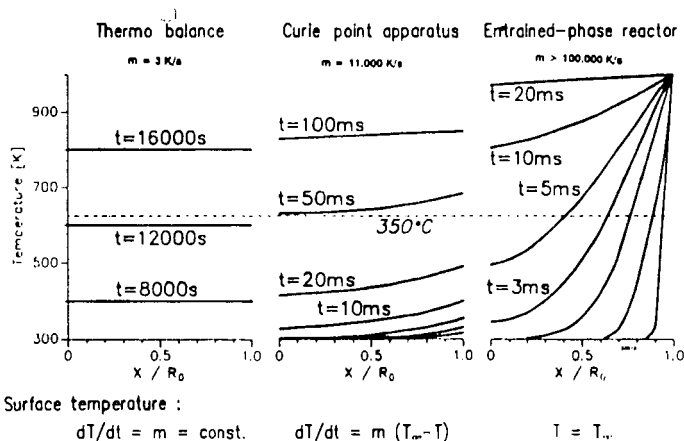


Fig. 5: Internal Profiles at and above Critical Radius d_k



Surface temperature :

$$dT/dt = m = \text{const.}$$

$$dT/dt = m (T_{\infty} - T)$$

$$T = T_{\infty}$$

Fig. 6: Intra - Particle Temperature Gradients at Different Experimental Conditions